



CATALYST RESEARCH CORPORATION

TEST EVALUATION OF  
FUEL CELL CATALYSTS

by

H. J. Goldsmith  
J. R. Moser  
T. Webb

Q-2

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### SUMMARY

The objective of this work is to test materials prepared by the Pittsburgh Coal Research Center for NASA as anodic catalysts for ammonia in 30% KOH and carbon monoxide in 2 N H<sub>2</sub>SO<sub>4</sub> and pH 3 acetate buffer fuel-cell electrolytes.

Corrosion potentials of each material were run in these three electrolytes. Surface areas were determined by double layer capacitance. Current versus voltage measurements at 25°C showed that two nickel-silver containing materials (RAL-10 and 32 NC) had utilizations (ma/gm) with carbon monoxide in acetate electrolyte twice that of platinum in the same electrolyte. However, they were only about 5% as active as platinum was in 2 N H<sub>2</sub>SO<sub>4</sub>. Unfortunately, as the exchange currents increased the half-cell potentials versus DHE also increased.

Three iron materials gave good potentials and high current densities for CO. Crushing them increased the surface areas between 16 and 500 times although the utilizations were no more than doubled. This is attributed to electrode flooding.

Six of the best catalysts for ammonia were found to be stable in KOH, but dissolved spontaneously upon addition of ammonia. Of those remaining, the best one (27 C) was only about 1-1/2% as active as platinum in KOH.

This work is being carried out for the National Aeronautics and Space Administration with Mr. E. M. Cohn as technical Monitor.

Principal investigators are Mr. T. Webb and Mr. J. R. Moser.

### INTRODUCTION

The second group consisting of twenty-two nickel and cobalt materials have been tested. Included were Raney cobalt and Raney nickel, five Raney alloys, eight carbides and seven nitrocarbides. Tests for anodic activity were conducted at 25°C with ammonia in 30% KOH and carbon monoxide in pH 3 acetate buffer and 2 N H<sub>2</sub>SO<sub>4</sub>. Nine iron materials were found to be stable in acetate buffer. This electrolyte generally gave better potential, although the conductivity and currents were lower. All the equipment and testing procedures have been described previously (1).

### TREATMENT OF CATALYSTS

These materials were inducted by washing with petroleum ether, acetone, methanol and water. They were stored under water overnight during which time gas bubbles were released. After drying, screen electrodes were prepared as before (1). All of the Raney materials gave high corrosion currents in all electrolytes tested. Leaching the electrodes with 30% KOH removed residual aluminum after which no corrosion current in alkali was observed.

Three iron samples (10 C, 23 C, and 1 CN) which showed the highest current densities for carbon monoxide were crushed with a six-ton press and ground with an agate mortar and pestle.

### RESULTS

Data obtained from voltammograms run with compatible catalyst-electrolyte combinations are shown in Tables I through XVI. Four of these tested (33 C, 43 C, 46 C, and 28 NC plus the two iron materials 5 CN and 12 C), however, dissolved upon the addition of ammonia. Materials which dissolved in 30% KOH, 2 N H<sub>2</sub>SO<sub>4</sub> and pH 3 acetate buffer are listed, with their surface areas, in Table XVII. Voltammetric data of the nine iron materials which did not dissolve are given in Table XVIII. Since low surface areas were found for all iron materials, three were crushed and run again. A comparison of these before and after crushing is shown in Table XIX.

### DISCUSSION

Of these twenty-two catalyst samples nineteen catalyst-electrolyte combinations were compatible. Eight were stable in 30% KOH, excluding those which dissolved upon addition of the ammonia, one in 2 N H<sub>2</sub>SO<sub>4</sub> and ten in pH 3 acetate buffer.

Catalyst surface areas were much higher for this group than for the iron materials. Values ranged from 2,700 cm<sup>2</sup>/gm for 21 NC to 11.7 m<sup>2</sup>/gm for 29 C with no apparent correlation between composition and surface.

When ammonia was added to KOH the four materials with the best utilizations were found to dissolve. The highest utilization of the remaining materials was only about 1-1/2% that found for platinum with ammonia. Sample 12 C which was reported previously

(1) as the most active iron material and 5 CN were also found to dissolve when ammonia was added.

Better results were obtained with carbon monoxide. Nitrocarbide 32 NC (3 Ni/1Ag) and Raney alloy RAL-10 (1Ni/1Co/1Ag) showed the highest utilizations, about twice that of platinum black when all three were run in acetate buffer. However, the best exchange current utilization obtained so far has been platinum black in 2 N H<sub>2</sub>SO<sub>4</sub>. This was approximately 40 times greater than when acetate was used. It was not possible to test the nickel-silver materials in sulfuric acid since all the nickel and cobalt materials except RN-2 reacted with this electrolyte.

Of the iron materials which had not been previously tested in acetate buffer, nine were found to be stable in this electrolyte. The carbide 10 C exhibit an exchange current density of 369  $\mu\text{a}/\text{cm}^2$ , higher than any other material tested. Since this catalyst consisted of large particles with a low surface area, it was assumed that by decreasing the particle size it might be possible to increase the utilization from one-fourth that of platinum to a higher value. The results were only partly successful; by crushing and grinding the surface was increased by a factor of 500, but the exchange utilization was only increased by 50%. Another carbide, 23 C and a carbonitride, 1 CN were also crushed and retested with similar results. One possible factor is electrode flooding with the smaller particle size. This may be alleviated by changing the PTFE-catalyst ratio or by adding certain inert materials.



### CONCLUSIONS

None of the nickel or cobalt materials appeared to be very good catalysts for ammonia oxidation, although some were three times as good as the iron catalysts. For carbon monoxide two nickel-silver materials (RAL-10 and 32 NC) looked promising and three iron materials (10 C, 23 C and 1 NC) may be potentially good catalysts with increased surface areas. Acetate electrolyte buffered at pH 3 gives better potentials and less corrosion than 2 N H<sub>2</sub>SO<sub>4</sub>, the expense being lower currents.

### RECOMMENDATIONS

The five best materials for carbon monoxide oxidation, RAL-10, 32 NC, 10 C, 23 C, and 1 NC, should be studied further.

REFERENCE

- (1) Goldsmith, H. J., J. R. Moser, and T. Webb, "Test Evaluation of Fuel Cell Catalysts", Quarterly Report Q-1 for period February 15, 1967 to May 15, 1967, Contract NASW - 1577, Catalyst Research Corporation, Baltimore, Maryland 21209

TABLE I

RC-1 Raney Cobalt

Surface Area	5,300 cm <sup>2</sup> /gm		
Fuel	NH <sub>3</sub>	CO	
Electrolyte	KOH	Acetate	
Limiting Current			
@ Volts	0.68	0.31	1.20
ma/gm	9.61	15.9	61.85
μa/cm <sup>2</sup>	1.82	3.00	11.67
Exchange Current			
@ Volts	0.54	0.29	1.06
ma/gm	1.35	0.60	1.13
μa/cm <sup>2</sup>	0.255	0.113	0.213
Tafel Slope	0.12	0.05	0.12

TABLE II

RN-2 Raney Nickel

Surface Area	5,300 cm <sup>2</sup> /gm				
Fuel	NH <sub>3</sub>	CO		CO	
Electrolyte	KOH	H <sub>2</sub> SO <sub>4</sub>		Acetate	
Limiting Current					
@ Volts	0.67	0.42	1.18	0.54	1.14
ma/gm	11.7	7.42	38.9	5.30	12.37
μa/cm <sup>2</sup>	2.21	1.40	7.33	1.00	2.33
Exchange Current					
@ Volts	0.54	0.38	0.99	0.50	1.08
ma/gm	1.42	0.71	2.12	0.71	3.89
μa/cm <sup>2</sup>	0.269	0.133	0.40	0.133	0.734
Tafel Slope	0.12	0.03	0.08	0.08	0.08

TABLE III

RAL - 6 Raney Alloy 3 Ni/ 1 Ag

Surface Area	26,900 cm <sup>2</sup> /gm
Fuel	NH <sub>3</sub>
Electrolyte	KOH
Limiting Current	
@ Volts	0.68
ma/gm	8.90
μa/cm <sup>2</sup>	0.331
Exchange Current	
@ Volts	0.54
ma/gm	1.78
μa/cm <sup>2</sup>	0.0225
Tafel Slope	0.14

TABLE IV

RAL - 8 Raney Alloy 1 Co/ 1 Ag

Surface Area	69,800 cm <sup>2</sup> /gm
Fuel	NH <sub>3</sub>
Electrolyte	KOH
Limiting Current	
@ Volts	0.69
ma/gm	9.61
μa/cm <sup>2</sup>	1.138
Exchange Current	
@ Volts	0.54
ma/gm	1.57
μa/cm <sup>2</sup>	0.0225
Tafel Slope	0.13

TABLE V

RAL - 9 Raney Alloy 3 Co/ 1 Ag

Surface Area	3,090 cm <sup>2</sup> /gm		
Fuel	NH <sub>3</sub>	CO	
Electrolyte	KOH	Acetate	
Limiting Current			
@ Volts	0.67	0.46	0.85
ma/gm	6.76	1.70	18.91
μa/cm <sup>2</sup>	2.19	0.55	6.11
Exchange Current			
@ Volts	0.54	0.35	0.73
ma/gm	1.07	0.354	4.24
μa/cm <sup>2</sup>	0.346	0.115	1.37
Tafel Slope	0.13	0.15	0.16

TABLE VI

RAL - 10 Raney Alloy 1 Ni/ 1 Co/ 1 Ag

Surface Area	6,200 cm <sup>2</sup> /gm		
Fuel	NH <sub>3</sub>	Co	
Electrolyte	KOH	Acetate	
Limiting Current			
@ Volts	0.70	0.44	0.87
ma/gm	5.70	55.84	169.6
μa/cm <sup>2</sup>	0.920	9.01	27.4
Exchange Current			
@ Volts	0.56	0.33	0.58
ma/gm	0.712	30.04	95.4
μa/cm <sup>2</sup>	0.115	4.85	15.4
Tafel Slope	0.07	0.40	0.25



TABLE VII

RAL - 11 Raney Alloy 1 Ni/ 1 Co/ 1 Au

Surface Area	9,700 cm <sup>2</sup> /gm		
Fuel	NH <sub>3</sub>	CO	
Electrolyte	KOH	Acetate	
Limiting Current			
@ Volts	0.68	0.46	0.85
ma/gm	8.20	81.6	91.9
μa/cm <sup>2</sup>	0.845	8.42	9.47
Exchange Current			
@ Volts	0.54	0.35	0.48
ma/gm	1.28	16.9	25.4
μa/cm <sup>2</sup>	0.132	1.75	2.62
Tafel Slope	0.14	0.14	0.70

TABLE VIII

27 C Carbide 3 Ni/ 1 Co

Surface Area	7,060 cm <sup>2</sup> /gm
Fuel	NH <sub>3</sub>
Electrolyte	KOH
Limiting Current	
@ Volts	0.32
ma/gm	40.6
μa/cm <sup>2</sup>	5.76
Exchange Current	
@ Volts	0.26
ma/gm	14.1
μa/cm <sup>2</sup>	2.00
Tafel Slope	0.12

TABLE IX

33 C Carbide Co

Surface Area	4,920 cm <sup>2</sup> /gm
Fuel	NH <sub>3</sub> *
Electrolyte	KOH
Limiting Current	
@ Volts	0.27
ma/gm	1,067.
μa/cm <sup>2</sup>	217.
Exchange Current	
@ Volts	0.22
ma/gm	106.
μa/cm <sup>2</sup>	21.6
Tafel Slope	0.04

\* - Electrode soluble in the presence of ammonia

TABLE X

35 C Carbide Ni

Surface Area	54,400 cm <sup>2</sup> /gm
Fuel	CO
Electrolyte	Acetate
Limiting Current	
@ Volts	0.80
ma/gm	45.2
μa/cm <sup>2</sup>	0.832
Exchange Current	
@ Volts	0.48
ma/gm	7.42
μa/cm <sup>2</sup>	0.136
Tafel Slope	0.14

TABLE XI

43 C Carbide 1 Ni/ 1 Ag

Surface Area	13,650 cm <sup>2</sup> /gm			
Fuel	NH <sub>3</sub> *		CO	
Electrolyte	KOH		Acetate	
Limiting Current				
@ Volts	0.39	0.75	0.75	0.96
ma/gm	212.	247.	54.8	113.
μa/cm <sup>2</sup>	15.5	18.1	4.01	8.28
Exchange Current				
@ Volts	0.30	0.68	0.59	0.72
ma/gm	42.4	60.1	13.4	20.5
μa/cm <sup>2</sup>	3.11	4.40	0.98	1.50
Tafel Slope	0.12	0.08	0.18	0.27

\* - Electrode soluble in the presence of ammonia

TABLE XII

46 C Carbide 3 Ni/ 1 Ag

Surface Area	4,050 cm <sup>2</sup> /gm	
Fuel	NH <sub>3</sub> *	CO
Electrolyte	KOH	Acetate
Limiting Current		
@ Volts	0.31	0.58
ma/gm	336.	57.2
μa/cm <sup>2</sup>	82.9	14.1
Exchange Current		
@ Volts	0.24	0.50
ma/gm	42.4	6.36
μa/cm <sup>2</sup>	10.5	1.57
Tafel Slope	0.08	0.07

\* - Electrode soluble in the presence of ammonia

TABLE XIII

15 NC Nitrocarbide 3 Ni/ 1 Co

Surface Area		6,900 cm <sup>2</sup> /gm		
Fuel		NH <sub>3</sub>		CO
Electrolyte		KOH		Acetate
Limiting Current				
@ Volts		0.36	0.68	0.72
ma/gm		6.36	9.90	18.0
μa/cm <sup>2</sup>		0.914	1.42	2.59
Exchange Current				
@ Volts		0.19	0.56	0.46
ma/gm		3.53	3.53	3.00
μa/cm <sup>2</sup>		0.507	0.507	0.431
Tafel Slope		0.65	0.23	0.17

TABLE XIV

23 NC Nitrocarbide Ni

Surface Area	19,800 cm <sup>2</sup> /gm
Fuel	CO
Electrolyte	Acetate
Limiting Current	
@ Volts	0.75
ma/gm	240.
μa/cm <sup>2</sup>	12.1
Exchange Current	
@ Volts	0.46
ma/gm	24.7
μa/cm <sup>2</sup>	1.25
Tafel Slope	0.12



TABLE XV

28 NC Nitrocarbide 1 Ni/ 1 Co

Surface Area	29,200 cm <sup>2</sup> /gm	
Fuel	NH <sub>3</sub> *	
Electrolyte	KOH	
Limiting Current		
@ Volts	0.33	0.40
ma/gm	84.8	88.4
μa/cm <sup>2</sup>	2.90	3.03
Exchange Current		
@ Volts	0.25	0.32
ma/gm	16.6	28.3
μa/cm <sup>2</sup>	0.569	0.968
Tafel Slope	0.10	0.13

\* - Electrode soluble in the presence of ammonia

TABLE XVI

32 NC Nitrocarbide 3 Ni/ 1 Ag

Surface Area	78,400 cm <sup>2</sup> /gm	
Fuel	CO	
Electrolyte	Acetate	
Limiting Current		
@ Volts	0.68	0.87
ma/gm	173.2	290.
μa/cm <sup>2</sup>	2.21	3.70
Exchange Current		
@ Volts	0.51	0.67
ma/gm	45.9	97.2
μa/cm <sup>2</sup>	0.586	1.24
Tafel Slope	0.25	0.30

TABLE XVII

## Surface Areas of Corroding Materials

29 C	Carbide	1 Ni/3 Ag	117,000 cm <sup>2</sup> /gm
39 C	Carbide	1 Co/1 Ag	20,200 cm <sup>2</sup> /gm
42 C	Carbide	1 Ni/1 Co	10,400 cm <sup>2</sup> /gm
21 NC	Nitrocarbide	Co	2,700 cm <sup>2</sup> /gm
22 NC	Nitrocarbide	3 Co/1 Ag	36,300 cm <sup>2</sup> /gm
26 NC	Nitrocarbide	1 Co/1 Ag	45,500 cm <sup>2</sup> /gm

TABLE XVIII

Iron Catalysts with CO in Acetate Electrolyte @ 25°C

<u>Material</u>	<u>Limiting Current</u>			<u>Exchange Current</u>			
	<u>Volts</u>	<u>ma/gm</u>	<u>μa/cm<sup>2</sup></u>	<u>Volts</u>	<u>ma/gm</u>	<u>μa/cm<sup>2</sup></u>	<u>Slope</u>
Pt	0.76	600.	3.48	0.21	47.6	0.284	0.31
1 NC	0.55	1.06	10.9	0.41	0.35	3.59	0.28
	1.18	6.36	65.2	0.98	1.13	11.6	0.18
4 CN	0.76	1.24	7.95	0.46	0.233	1.49	0.21
	1.25	5.48	35.1	1.05	0.813	5.21	0.14
4 NC	0.65	1.77	64.3	0.48	0.530	19.2	0.24
	1.24	4.95	179.	1.04	0.848	30.7	0.18
5 CN	1.20	8.48	156.	0.41	0.424	7.82	0.15
10 C	0.54	110.	3,291.	0.31	12.4	369.	0.14
12 C	0.80	1.06	32.2	0.36	0.219	6.66	0.38
	1.25	3.53	107.	1.06	0.565	17.2	0.14
18 N	1.13	9.37	113.	1.00	1.77	21.4	0.12
21 N	0.60	1.13	15.3	0.32	0.106	1.43	0.10
	1.24	5.30	71.6	1.03	1.13	15.3	0.16
23 C	0.64	19.4	717.	0.36	1.76	65.0	0.09

TABLE XIX

## Effect of Crushing on Some Iron Catalysts

Material	10 C		23 C		1 CN	
Surface Area (cm <sup>2</sup> /gm)	33.5	14,680.	27.1	7,950	46.0	809.
Fuel	CO	CO	CO	CO	CO	CO
Electrolyte	Acetate		Acetate		2 <u>N</u> H <sub>2</sub> SO <sub>4</sub>	
Limiting Current						
@ Volts	0.54	0.36	0.64	0.56	1.13	1.10
ma/gm	110.3	60.7	19.4	14.8	70.8	180.
μa/cm <sup>2</sup>	3,291.	4.14	717.	1.86	1.530.	223.
Exchange Current						
@ Volts	0.31	0.30	0.36	0.40	0.50	0.63
ma/gm	12.4	18.7	1.76	3.24	36.4	9.88
μa/cm <sup>2</sup>	369.	1.27	65.0	0.407	790.	12.2
Tafel Slope	0.14	0.08	0.09	0.20	2.20	0.18

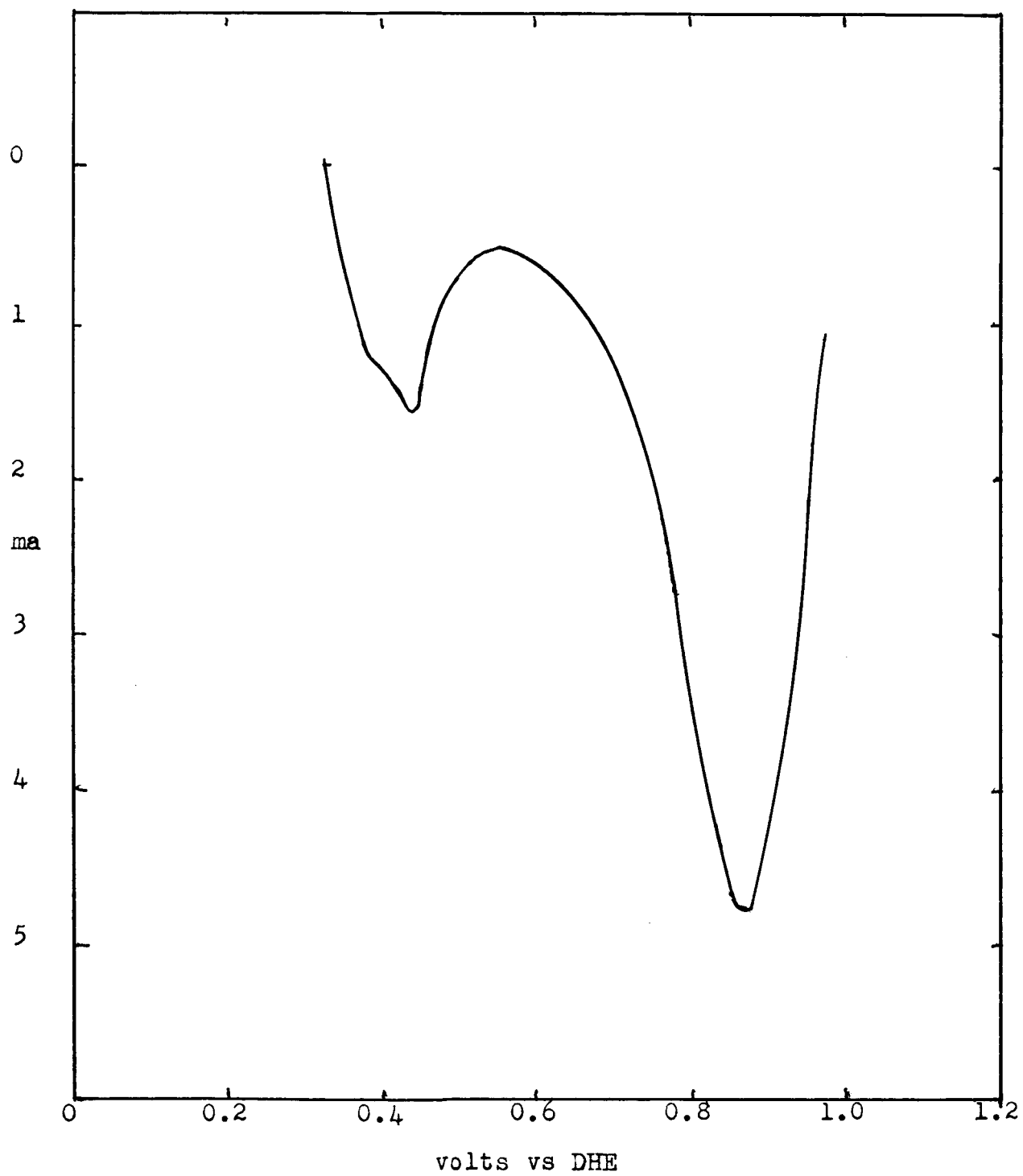


Figure 1  
E vs i for RAL-10

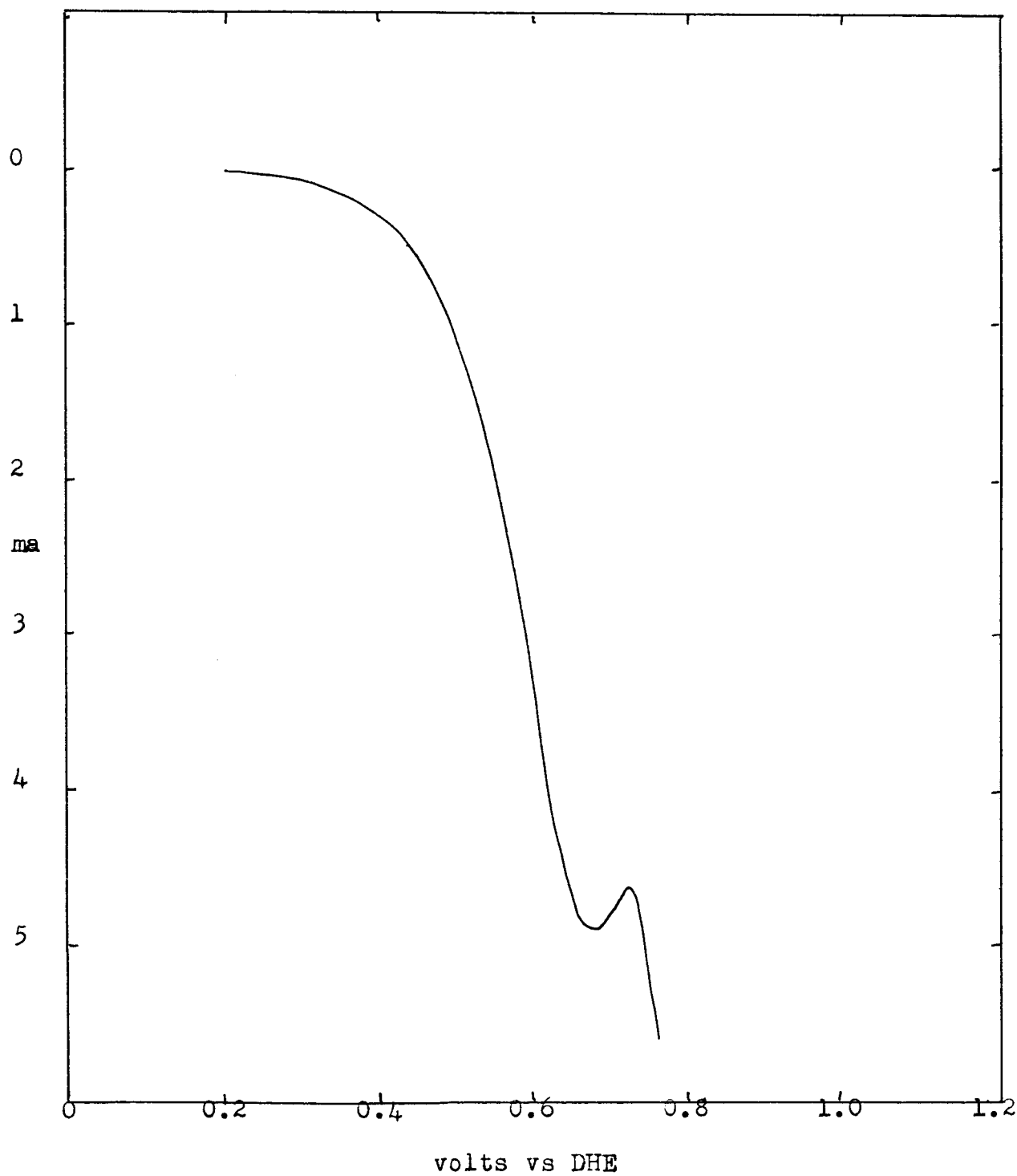


Figure 2

E vs i for 32 NC

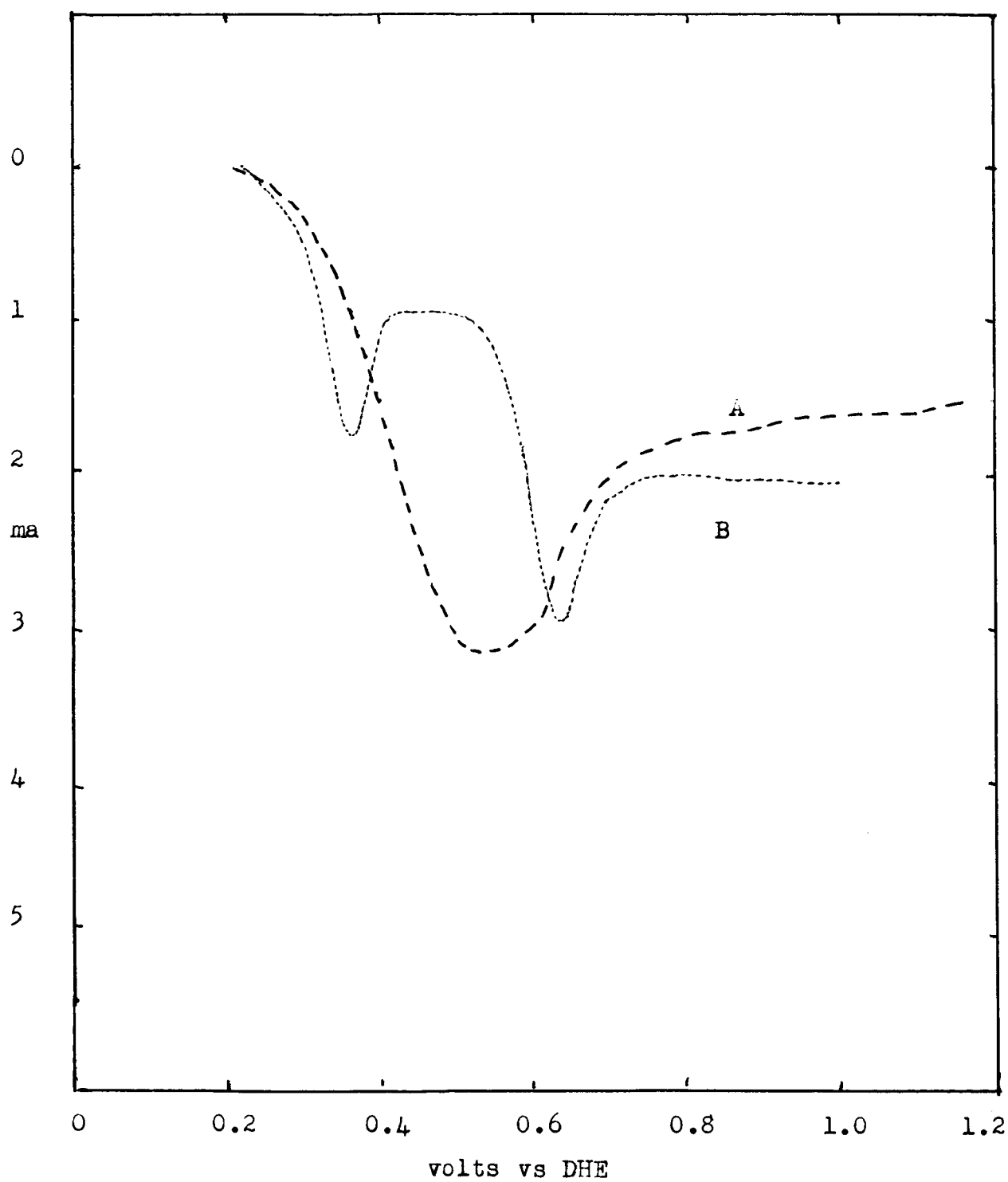


Figure 3

E vs i for 10 C

(A) Small surface, (B) Large surface



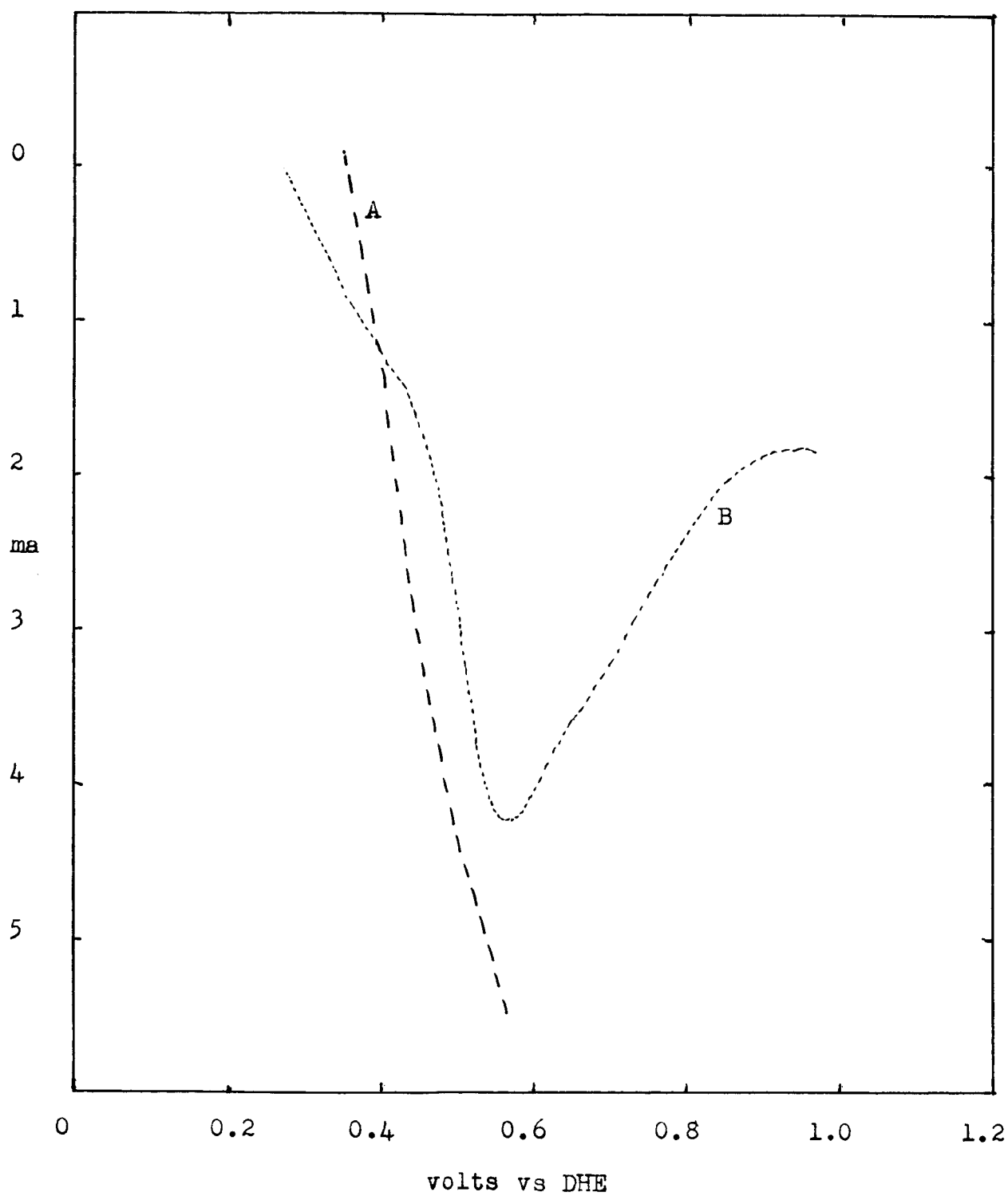


Figure 4

E vs i for 23 C  
(A) Small surface, (B) Large surface



CATALYST RESEARCH CORPORATION

August 24, 1967

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